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(54) RESIN COMPOSITION FOR PRINT LAMINATE

(57)Abstract:

PURPOSE: To obtain a film for print laminate which exhibits good low-temp. adhesive properties and good adhesion to a printing ink.

CONSTITUTION: A film for print laminate is obtd. by laminating, to a plastic film, a resin compsn. which has a melt flow rate (190°C) of 10-80g/10min and is obtd. by compounding 50-90wt.% ethylene-unsatd. ester copolymer having an unsatd. ester content of 10-40wt.% with 8-40wt.% tackifier and 2-10wt.% thermoplastic vinylarom. hydrocarbon-olefin block copolymer.

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MEANS

[Means for Solving the Problem] As a result of this invention persons' repeating examination wholeheartedly in view of the above-mentioned present condition, by adding the thermoplastic block copolymer which becomes the constituent which consists of the copolymer and tackifier of ethylene and unsaturation ester from a vinyl aromatic compound and a conjugated-diene compound, it finds out solving the aforementioned technical problem and came to complete this invention.

[0006] That is, this invention relates to the resin constituent for a print lamination which came to blend 2 - 10 % of the weight of thermoplastic block copolymers which consist of the copolymer 50 of the ethylene and unsaturation ester whose content of (1) unsaturation ester is 10 - 40 % of the weight - 8 - 40 % of the weight of (2) tackifiers, and (3) vinyl aromatic hydrocarbon and an olefin 90% of the weight, and was excellent in the low-temperature adhesive property and bond strength whose melt flow rates (190 degrees C) are 10 - 80g / 10 minutes. Furthermore, it is related with the film for a print lamination which comes to carry out the laminating of this resin constituent to plastic film.

[0007] As unsaturation ester in the copolymer of the (1) ethylene and unsaturation ester which are used as a component of the resin constituent of this invention, unsaturation carboxylates, such as a methyl of vinyl esters, such as vinyl acetate, a propionic-acid vinyl, and a benzoic-acid vinyl, and an acrylic acid, or a methacrylic acid, ethyl, n-butyl, and isobutyl ester, can be mentioned. In this, especially the copolymer of desirable ethylene and desirable unsaturation ester is an ethylene vinylacetate copolymer.

[0008] The unsaturation ester content in the copolymer of ethylene and unsaturation ester is 15 - 20 % of the weight preferably ten to 40% of the weight. If the low-temperature adhesive property of this resin constituent and a bond strength become [an unsaturation ester content] bad at less than 10 % of the weight and an unsaturation ester content exceeds 40 % of the weight, trouble, such as generating of the volume blocking at the time of blocking of this resin constituent becoming large, carrying out the extrusion lamination of the inconvenience on the handling at the time of supplying this resin constituent to generating of blocking under stock of this resin constituent and an extruder and this resin constituent at plastic film, and producing the film for a print lamination, will arise.

[0009] As (2) tackifiers used as a component of the resin constituent of this invention, an aliphatic system hydrocarbon resin, an alicycle-like system hydrocarbon resin, an aromatic system hydrocarbon resin, a polyterpene system resin, rosin, a styrene resin, etc. can be mentioned.

[0010] As an example of an aliphatic system hydrocarbon resin, butene-1, an isobutylene, a butadiene, The polymer which makes a principal component C4 - C5 monochrome or diolefins, such as 1 and 3-pentadiene The resin which carried out cyclization dimerization

postpolymerization of the diene component in SUPENTO C4 - C5 fraction as an example of an alicycle-like system hydrocarbon resin, The resin, hydrogenation dicyclopentadiene resin to which the polymerization of the annular monomers, such as a cyclopentadiene, was carried out, As an example of aromatic system hydrocarbon resins, such as a resin which carried out hydrogenation in a nucleus of the aromatic system hydrocarbon resin, vinyltoluene, The resin which made the principal component C9 vinyl aromatic hydrocarbons, such as an indene and an alpha methyl styrene As an example of a polyterpene system resin, an alpha pinene polymer, beta-pinene polymer, A dipentene polymer, a terpene-phenol copolymer, an alpha pinene-phenol copolymer, etc., As an example of rosin, rosin, polymerization rosin, hydrogenation rosin, a rosin glycerol ester and its hydrogenation object, or a polymerization object, As an example of styrene resins, such as rosin pentaerythritol ester and its hydrogenation object, or a polymerization object, the polymer of a styrene system monomer, a vinyltoluene-alpha-methyl-styrene copolymer, etc. are mentioned. In these various tackifiers, an alicycle-like system hydrocarbon resin and a terpene system resin are preferably used from points, such as a color tone and an odor.

[0011] Furthermore, the thermoplastic block copolymer which consists of a (3) vinyl aromatic hydrocarbon used as a component of the resin constituent of this invention and an olefin The following general formula (A-B) n , n -A(A-B) $'$, or (A-B) m -X (however, in an olefin polymer block and n , the integer of 1-5 and m express the integer of 2-7, and, as for the inside A of a formula, and A', X expresses [a vinyl aromatic-hydrocarbon polymer block and B] the polyfunctional compound of m ** .) It is the polymer which has the block structure which consists of the straight chain structure, the radiated structure, or branching structure expressed, and whose piece end is a vinyl aromatic-hydrocarbon polymer block at least. As an example of the vinyl aromatic hydrocarbon used here, styrene, an alpha methyl styrene, vinyltoluene, p-tert-butyl styrene, a vinyl xylene, an ethyl vinyl xylene, vinyl naphthalene, such mixture, etc. are mentioned. Especially among these, styrene is desirable. On the other hand as an example of an olefin, alpha olefins, such as conjugate diolefins, such as a butadiene and an isoprene, and ethylene, a propylene, and 1-butene, etc. are mentioned. Moreover, what hydrogenated the polymer block which carried out the polymerization of the conjugate diolefin as this component (3) may be used, and further, Block B may use the copolymer of a conjugate diolefin and a vinyl aromatic hydrocarbon, as long as an olefin unit is superior. The amount of the vinyl aromatic-hydrocarbon polymer block in the thermoplastic block copolymer which consists of a vinyl aromatic hydrocarbon and an olefin is usually 10 - 40 % of the weight preferably eight to 55% of the weight. Among these, in this invention, the thermoplastic block copolymer which consists of a vinyl aromatic hydrocarbon which has a vinyl aromatic-hydrocarbon polymer block, and an olefin is desirable to both ends, and the hydrogenation object of a polystyrene-polybutadiene-polystyrene block copolymer is especially used for them preferably from the point of improvement in thermal stability. In addition, these thermoplasticity block copolymer is marketed (for example, Cali FREX (Cariflex) TR, Clayton (Kraton) G, Clayton D all Shell Chemistry company make).

[0012] For (1) component, 50 - (2) component is [8 - (3) component of each rate of (1) - (3) component described above] 2 - 10 % of the weight 40% of the weight 90% of the weight.

(1) If the processability at the time of a component extruding and laminating this resin constituent at less than 50 % of the weight becomes bad and exceeds 90 % of the weight, the bond strength to the printing ink used for printing paper etc. will become small. (2) If a component is inferior to the bond strength to printing ink and exceeds 40 % of the weight at less than 8 % of the weight, blocking of this resin constituent will become large and extrusion lamination nature will also become bad. (3) A bond strength with the ink in which a component is used for printing paper etc. at less than 2 % of the weight becomes small, and if a low-temperature adhesive property also becomes bad and it exceeds 10 % of the weight, as a result of the compatibility of this resin constituent becoming bad, extrusion lamination nature

becomes bad.

[0013] Moreover, JIS The 190-degree C melt flow rates (it may abbreviate to "MFR" hereafter) of this resin constituent by K6730 are 10-80g / 10 minutes. A bond strength becomes small, as a result of a permeate lump of the resin to the printing paper at the time of adhesion etc. being lost by MFR in 10g / less than 10 minutes, since the fluidity of a melting resin is bad. Since the fluidity of a melting resin is too high when MFR exceeds 80g / 10 minutes, in the usual working temperature, lamination nature must be bad, and, for this reason, must extrude at low temperature, and lamination must be carried out, consequently the bond strength to plastic film becomes small.

[0014] Although manufacture of the resin constituent of this invention can adopt various methods, such as the method of blending the solid-state-like component of (1) - (3) in the state of melting using the method and extruder which are mixed mechanically, a Banbury mixer, a kneader, etc., and the method of blending in the state of a solution, the method of blending in the state of melting using an extruder is the most suitable for it.

[0015] Although especially the method of producing the film for a print lamination using the resin constituent of this invention is not limited, it can mention the method of extruding and laminating the resin constituent of this invention in the plastic film used as a base material, the method of co-extruding the resin constituent of a resin and this invention used for plastic film, etc. before and after carrying out the laminating of this resin constituent to plastic film if needed -- a film -- one shaft -- or you may carry out biaxial extension. Although especially the thickness of the base-material plastic film layer of the film for a print lamination is not limited, it is 10-30 micrometers preferably 5-100 micrometers. Moreover, the thickness of the resin constituent layer of this invention has desirable 2-30 micrometers. You may perform surface treatment, such as a corona treatment and a flame treatment, to plastic film before and after carrying out the laminating of this resin constituent to plastic film, and/or this resin constituent after a laminating if needed.

[0016] The plastic film used as a base material of the film for a print lamination is films, such as polyolefines, such as a polypropylene system and a polyethylene system, polyester, a polyamide, and a polycarbonate, and polypropylene system films, such as a copolymer of polypropylene, a propylene, and other alpha olefins, are used suitably especially. Moreover, a basis film layer may be a multilayer.

[0017] In the plastic film used as a base material, and the resin constituent of this invention, a book an

EXAMPLE

[Example] Next, although an example explains this invention still more concretely, this invention is not limited to these.

[0019] example 1 ethylene vinylacetate copolymer (vinyl acetate content; -- 15% of the weight) it may abbreviate to "EVA" below for MFR; 14g /, and 10 minutes 74.8% (below the same% of the weight --) the alicycle-like system hydrocarbon resin (ring and ball method softening temperature; -- 100 degrees C) as a tackifier Tradename; ARUKON P-100 (product made from Arakawa Chemistry) 20%, and polystyrene-polyethylene / butylene-polystyrene block copolymer (by the hydrogenation object of a polystyrene-polybutadiene-polystyrene block copolymer, it may abbreviate to "SEBS" below) Styrene block content; erucic-acid amide 0.2% was added to 13% and tradename; Clayton G1657 (product made from Shell Chemistry) 5%, melting mixture was carried out using the biaxial extruder, and it considered as the pellet. MFRs of this constituent were 42g / 10 minutes.

[0020] With the extruder of the diameter of 25mm, melting extrusion of this constituent pellet was carried out to the corona-treatment side of a biaxial extension polypropylene resin film

(20-micrometer thickness) from the T die, it extruded on the resin temperature of 200 degrees C, and 20m a part for /and the conditions of 13 micrometers of coating thickness of working speeds, and lamination was performed. It did not exfoliate easily between this resin constituent and the base-material film.

[0021] The obtained laminate film was heat sealed to the printing side of coat paper on the temperature of 70-95 degrees C, pressure 2 Kg/cm², and the heat-sealing conditions for time 0.5 seconds, and the bond strength (180-degree peel strength) was measured. Although these results were shown in Table 1 and drawing 1, the resin constituent of this invention was what has a good bond strength also to which ink used for printing paper etc., and is excellent in the low-temperature adhesive property.

[0022] Erucic-acid amide 0.2% was added to 20% (ring and ball method softening temperature; 100 degrees C, tradename; ARUKON P-100 (product made from Arakawa Chemistry)) of alicycle-like system hydrocarbon resins as example of comparison 1 EVA(vinyl acetate content; MFR;14g / [15 % of the weight and], 10 minutes)79.8%, and a tackifier, melting mixture was carried out using the biaxial extruder, and it considered as the pellet. MFRs of this constituent were 43g / 10 minutes.

[0023] Although the above-mentioned constituent pellet was extruded and laminated by the same method as an example 1 on the same base-material film as an example 1, it did not exfoliate easily between this resin constituent of this and the base-material film. Moreover, the laminate film obtained like the example 1 was heat sealed to the printing side of coat paper, and the bond strength was measured. Although these results were shown in Table 1 and drawing 1, the resin constituent of the example 1 of comparison was what whose a bond strength is weak and is inferior also to a low-temperature adhesive property to the ink used for printing paper etc.

[0024] As an example 2 thermoplasticity block copolymer, using the same constituent component as an example 1, melting mixture was carried out with the biaxial extruder by the same blending ratio of coal, and the pellet was produced except having used the polystyrene-polyisoprene-polystyrene block copolymer (styrene block content; 15%, tradename; Cali FREX KX400 P (Shell Chemistry company make)). MFRs of this constituent were 42g / 10 minutes.

[0025] Although this constituent pellet was extruded and laminated like the example 1 on the same base-material film as an example 1, it did not exfoliate easily between this resin constituent and the base-material film. Moreover, the laminate film obtained like the example 1 was heat sealed to the printing side of coat paper, and the bond strength was measured. Although these results were shown in Table 1, the resin constituent of this example was what whose a bond strength is strong and is excellent in the low-temperature adhesive property to the ink used for printing paper etc.

[0026] 0.2% of oleic amide was added to the same SEBS5% as 79.8% (ethyl-acrylate content; MFR;20g / [20% and], 10 minutes) of example 3 ethylene-ethyl-acrylate copolymers, 15% (ring and ball method softening temperature; 115 degrees C, tradename; YS resin Px1150 (product made from Yasuhara Fats and oils)) of terpene resins as a tackifier, and an example 1, melting mixture was carried out using the biaxial extruder, and it considered as the pellet. MFRs of this constituent were 45g / 10 minutes.

[0027] Melting extrusion of this constituent pellet was carried out to the polyethylene side of polyester (12-micrometer thickness) / polyethylene (10-micrometer thickness) two-layer film from the T die with the extruder of the diameter of 25mm, it extruded on the resin temperature of 200 degrees C, and 20m a part for /and the conditions of 13 micrometers of coating thickness of working speeds, and lamination was performed. It did not exfoliate easily between this resin constituent and the base-material film.

[0028] The laminate film obtained like the example 1 was heat sealed to the printing side of coat paper, and the bond strength was measured. Although these results were shown in Table

1, the resin constituent of this example was what whose a bond strength is strong and is excellent in the low-temperature adhesive property to the ink used for printing paper etc.

[0029] As an ethylene vinylacetate copolymer of example of comparison 2 example 1, except having used the vinyl acetate content of 7%, and the object for MFR20g / 10 minutes, the same constituent component as an example 1 was blended at same rate, melting mixture was carried out using the biaxial extruder, and it considered as the pellet. MFRs of this constituent were 55g / 10 minutes.

[0030] Although this constituent pellet was extruded and laminated like the example 1 on the same base-material film as an example 1, it did not exfoliate easily between this resin constituent and the base-material film. Furthermore, the laminate film obtained like the example 1 was heat sealed to the printing side of coat paper, and the bond strength was measured. Although these results were shown in Table 1, this resin constituent was what whose a bond strength is weak and is inferior to a low-temperature adhesive property to the ink used for printing paper etc.

[0031] As example of comparison 3EVA, except having used the vinyl acetate content of 42%, and EVA for MFR20g / 10 minutes, the same constituent component as an example 1 was blended at same rate, melting mixture was carried out with the kneader, and it considered as the pellet. MFRs of this constituent were 55g / 10 minutes.

[0032] When it was going to extrude and laminate this constituent pellet on the same base-material film as an example 1 like the example 1, since the pellet blocked, lamination was not completed on it.

[0033] The same constituent component as example of comparison 4 example 1 was blended as in Table 2, melting mixture was carried out with the kneader, and it considered as the pellet. MFR of this constituent was as in Table 2.

[0034] When it was going to extrude and laminate this constituent pellet on the same base-material film as an example 1 like the example 1, the lamination started and stabilized was not able to do a surging on it.

[0035] The same constituent component as five to example of comparison 6 example 1 was blended as in Table 2, melting mixture was carried out with the biaxial extruder, and it considered as the pellet. MFR of this constituent was as in Table 2.

[0036] When this constituent pellet was extruded and laminated like the example 1 on the same base-material film as an example 1, it did not exfoliate easily between these resin constituents and base-material films. Moreover, the laminate film obtained like the example 1 was heat sealed to the printing side of coat paper, and the bond strength was measured. Although these results were shown in Table 1, these resin constituents had the weak bond strength to the ink used for printing paper etc.

[0037] The same constituent component as example of comparison 7 example 1 was blended as in Table 2, melting mixture was carried out with the biaxial extruder, and it considered as the pellet. MFR of this constituent was as in Table 2.

[0038] When it was going to extrude and laminate this constituent pellet on the same base-material film as an example 1 like the example 1, the lamination started and stabilized was not able to do a surging on it.

[0039] As example of comparison 8EVA, except having used the vinyl acetate content of 20%, and EVA for MFR50g / 10 minutes, the same constituent component as an example 1 was blended at same rate, melting mixture was carried out with the kneader, and it considered as the pellet. MFRs of this constituent were 109g / 10 minutes.

[0040] Melting extrusion of this constituent pellet was carried out to the corona-treatment side of a biaxial extension polypropylene resin film (20-micrometer thickness) from the T die with the extruder of the diameter of 25mm, and when it extruded on the resin temperature of 200 degrees C, and 20m a part for /and the conditions of 13 micrometers of coating thickness of working speeds and lamination was performed, processing by which the surging in lamination

was occurred and stabilized was not completed. Although it was stabilized when resin temperature was lowered to 170 degrees C, and lamination was completed, this resin constituent exfoliated easily from the polypropylene film of a base material, and was hardly pasted up on a base material.

[0041] Example of comparison 9EVA(vinyl acetate content; MFR;1.5g / [15 % of the weight and], 10 minutes)82.8%, erucic-acid amide 0.2% was added to 10% (ring and ball method softening temperature of 100 degrees C, tradename; ARUKON P-100 (product made from Arakawa Chemistry)) of alicycle-like system hydrocarbon resins as a tackifier, and SEBS(styrene block content; 13%, tradename; made in Clayton G1657)7%, melting mixture was carried out using the biaxial extruder, and it considered as the pellet. MFRs of this constituent were 3.7g / 10 minutes.

[0042] Melting extrusion of this constituent pellet was carried out to the corona-treatment side of a biaxial extension polypropylene resin film (20-micrometer thickness) from the T die with the extruder of the diameter of 25mm, and when it extruded on the resin temperature of 240 degrees C, and 20m a part for /and the conditions of 13 micrometers of coating thickness of working speeds and lamination was performed, it did not exfoliate easily between this resin constituent and the base-material film.

[0043] The laminate film obtained like the example 1 was heat sealed to the printing side of coat paper, and the bond strength was measured. Although these results were shown in Table 1, the resin constituent of this example had the weak bond strength to the ink used for printing paper etc.